Effect of compressive strain in the phase separation of $La_{0.3}Ca_{0.7}$ MnO_3 ultrathin films

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Colossal magnetoresistance manganites, are complex systems with a rich phase diagram, in which a complicated interplay between oxygen doping, disorder and structural distortions may influence their tendency to phase separation [1]. Epitaxial strain and strain relaxation in thin films has been explored as a method to tailor structural distortions and examine its influence on the physical properties. However, depressed saturation magnetizations and reduced Curie temperatures are usually observed for nanometer thick layers both for compressive and tensile in plain stress [2], and a clear picture of the effect of strain related structural distortions has not emerged yet. In addition most studies are on films with thickness above 10 nm for which substantial strain relaxation may have occurred, and more importantly, structural features associated to strain relaxation may be overgrown and eventually smoothen out at this large thickness values. A structural characterization of ultrathin films with nanoscale thickness is thus of primary importance to establish the relative roles played by factors such as strain, doping and disorder on the modified physical properties of these complex oxides [3].

Here we report on the effect of epitaxial strain on ultrathin $La_{0.7}Ca_{0.3}MnO_3$ films grown by high pressure (3.4 mbar) dc sputtering technique in pure oxygen atmosphere and at elevated temperature (900ºC). Substrates were (100) oriented $SrLaAlO_4$ (SLAO) with an in plane lattice parameter of 0.375 nm. High in plane compressive strain (-3.1 %) is then induced in the LCMO with much larger bulk lattice parameter (0.387 nm). A structural study has been conducted using x-ray diffraction (XRD) and aberration corrected scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS).

For thicknesses below 6.5 nm, films are strained as measured by the expansion of c axis by means of XRD, and show a two dimensional growth . Films with a thickness above 6.5 nm show island growth indicating a relaxation of the structure, although some residual strain remains. STEM images with atomic resolution (0.13 nm) show a cell doubling superstructure along the growth direction in regions extending laterally over 2 – 20 nm as shown in Figure 1. EELS analysis of this ultrathin LCMO on SLAO evidences oxygen deficiency as revealed by the reduction of the oxygen K edge pre-peak. This oxygen vacancies are in consistent with the reduction of the Mn valence measured by the $L_{2,3}$ ratio, while the La/Ca relative stochyometry remains constant. We argue that the double periodicity results of oxygen vacancy ordering, although oxygen deficiency is also present for regions where the double periodicity is not revealed, as shown in Figure 2a and Figure 2b. This reduction of Mn valence to (less doped LCMO) triggers a more insulating behaviour as evidenced by transport measurements for films below the critical thickness. Interestingly, even for the thinnest 4 nm films analysed, saturation magnetizations as measured by SQUID magnetometer are in excess of 2 μ_B/Mn atom as typically found in thick (100 nm) films.

The picture arises that strain is accommodated by the creation of oxygen vacancies over nanometric regions. This drives the sample insulating (less doped) although it has little effect on the net saturation moment. Our result constitutes a direct evidence of strain induced phase separation caused by local variations of the oxygen content.

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[1] A. Moreo, S. Yunoki, E. Dagotto, Science **283**, 2034 (1999).
[2] M. Bibes, Ll. Balcells, S. Valencia, J. Fontcuberta, M. Wojcik, E. Jedryka, S. Nadolski, Phys. Rev. Lett. **87**, 67210 (2001).
[3] M. Varela, W. Grogger, D. Arias, Z. Sefrioui, C. León, L. Vazquez, C. Ballesteros, K. M. Krishnan, J. Santamaría, Phys. Rev. B **66**, 174514 (2002).

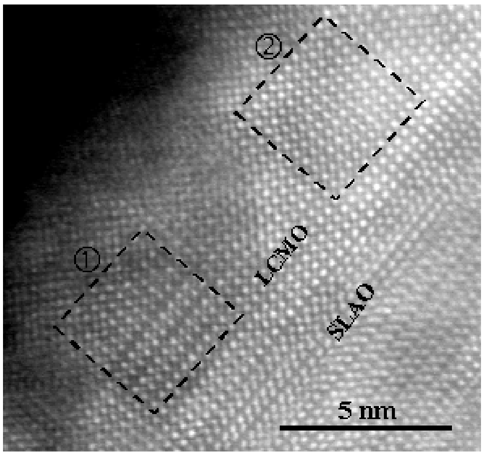

FIG. 1: Z-contrast image of the sample 6.5 nm thick, grown on SLAO, showing coherent and flat interface between substrate and film, and two different regions corresponding to a superstructured, labelled ①, and a normal, labelled ②, LCMO.

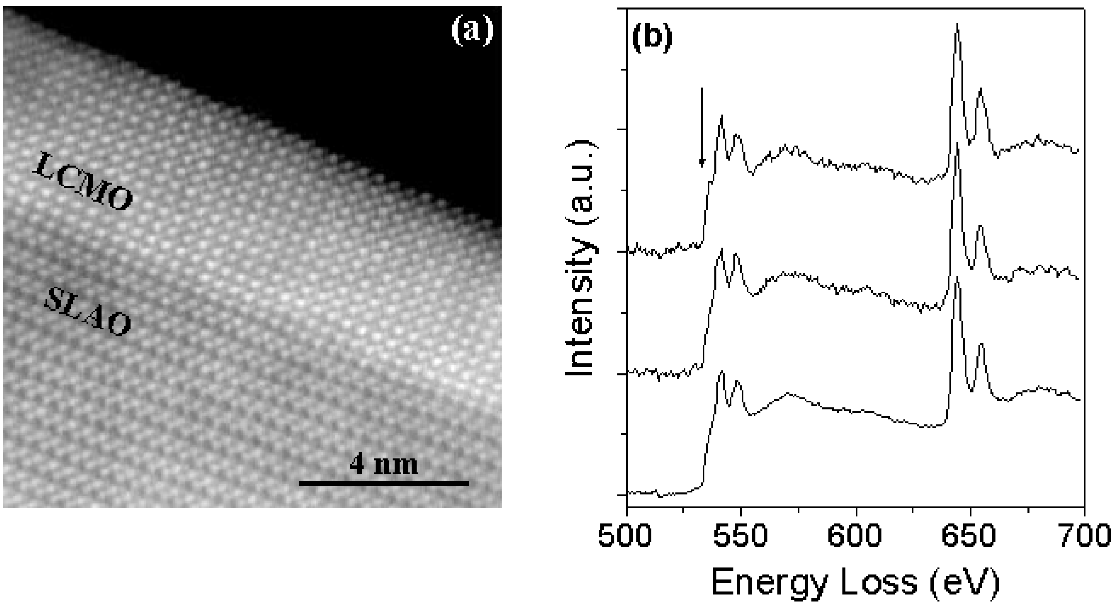

FIG. 2: (a) Z-contrast image of the sample 4 nm thick, where the superstructure is not revealed, (b) EEL spectra showing a depression of the O K-edge (marked with an arrow), which corresponds with an oxygen deficiency, and the L_3, L_2 lines of the Mn.